

# EFFECT of HYGROTHERMAL AGING HISTORY on SORPTION PROCESS, SWELLING and GLASS TRANSITION TEMPERATURE in a PARTICLE-FILLED EPOXY-BASED ADHESIVE

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## INTRODUCTION

The excellent mechanical properties of epoxy resins have led to their use as adhesives for structural bonding applications. However, the durability of adhesives, especially for those bonding metallic adherents, can be affected by environmental exposure. Humidity, ionic contaminants and temperature are all factors for degradation of structural bonding [Hand et al., 1991; Tai and Szklazska-Smialowska, 1996; Chiang and McKenna, 1996]. Water absorption and exposure to other environments degrade the mechanical strength and physical properties of the adhesives. The degradation may be strongly affected by the presence and nature of fillers within the adhesives, because the interface between resin and fillers can be preferentially attacked by the environmental agent. Therefore, knowledge of the behavior of adhesives under adverse conditions is necessary to predict their long-term performance. This work continues the investigation of a previous study [Chiang and Fernandez-Garcia, 1999] on the water sorption characteristics and measurements of swelling and the depression of the glass transition temperature ( $T_g$ ) of a particle-filled, epoxy-based structural adhesive. In the present study, a cycle of water absorption/desorption/reabsorption (ADR) in a commercial adhesive has been conducted to mimic environmental exposure in typical applications. Consequently the absorption of water by adhesives is generally not able to reach the saturation level, nor is desorption completed to the fully dry condition.

Although the mechanisms of diffusion of water into neat or filled polymer resins are still not completely understood, the problem is even more complex when the material is subjected to several water exposure cycles (ADR cycles). It has been found [Lee and Rockett, 1992] in unsaturated polyester, vinyl ester and acrylic resins that the diffusion coefficients,  $D$ , calculated for absorption were much higher than those for desorption and reabsorption, because the  $D$  of absorption was calculated using the "observed water content" which was lower than the "true water content." Lee and Knaebel (1997) performed experiments on fluoropolymers exposed to toluene and benzene solutions. Their results show that the diffusion coefficient in repeatedly exposed specimen appears to be consistently smaller than that of fresh samples. However, in a study of the methanol diffusion into poly-(methyl

methacrylate), Grinsted and Koenig (1992) found that the diffusivity increases with the number of cycles. All these investigations have been generally performed in neat resins (thermosets) or polymers (thermoplastics) without consideration of fillers. There are also some studies on the effect of hygrothermal cycles on the viscoelastic response of polymeric composites [Hilton and Yi, 1993; Yi and Hilton, 1995], but the cycle effect on the diffusion of moisture into the material was not analyzed. This work attempts to give some insight to the ADR behavior of a particle-filled epoxy-based commercial adhesive. The effects of hygrothermal aging history and initial water content on the structure and physical properties were examined. Also, the relation of swelling and  $T_g$  depression to the apparent free volume under ADR conditions was investigated.

## MATERIAL and EXPERIMENTAL PROCEDURES

The present study uses a gravimetric technique to characterize the sorption under hygrothermal aging at temperatures from 30 °C to 45 °C in distilled water. The adhesive used in this study is an epoxy-based structural adhesive supplied by 3M Corporation (3M 5042)<sup>1</sup> formulated for automotive hem and body structure applications [Yorkgitis and Marhevka, 1994]. Adhesive films, nominally 300  $\mu$ m thick, have been produced by curing the adhesive between Teflon blocks in a pressure vessel at 130 °C and 1.38 MPa (200 psi) for 13 h. The samples were then slowly cooled to room temperature. Such a procedure enables us to overcome the critical issue of preparing thin films with uniform thicknesses and no voids. DSC experiments have shown that the adhesive has a dry  $T_g$  of 86 °C (the standard uncertainty for the  $T_g$  measurements is  $\approx 3$  °C). After curing, the film was cut to dimensions of ca. 40 mm x 6 mm x 0.3 mm. The initial mass fraction of water in samples was less than 0.05 %,

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<sup>1</sup>Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply necessarily that they are the best available for the purpose.

and their initial dimensions were obtained using electronic calipers.

There were two reabsorption procedures adopted in this study. The first, Case I, was used after the removal of specimens (hygrothermally exposed in distilled water baths at constant temperatures of 30 °C, 35 °C, 40 °C and 45 °C) from the baths at different times (about 3-5 specimens per bath each time) to measure water uptake for absorption in virgin material. These samples were not put back into the bath for subsequent mass uptake measurements. Instead, a desorption (drying) procedure was conducted on them at the same temperature used in the absorption procedure. Drying process was continuously conducted in an oven at ambient pressure and humidity, and the mass of each specimen was periodically measured until reaching the final equilibrium state. By only drying the specimen at the initial hygrothermal aging temperature, we know that the water cannot be dried out completely; consequently, a small amount of water was retained in each specimen. Subsequently, these specimens with their “initial” water content remaining were placed back into the distilled water bath for the reabsorption process at their original aging temperature. The initial water content depends on the hygrothermal aging time in the absorption. During this reabsorption process, specimens were taken from the bath for water uptake measurements at the same time used in the absorption process.

The second procedure, Case II, was conducted on specimens that were completely dried after reaching saturation in the initial sorption procedure. These specimens were continuously exposed in distilled water baths at constant temperatures of 30 °C, 35 °C, 40 °C and 45 °C during the absorption process. After the specimens were saturated, they were completely dried in a vacuum oven at 60 °C. Afterwards, the specimens with zero water content were put back into distilled water baths at the same temperature used in absorption procedure for reabsorption. During the reabsorption procedure for Case II, specimens were taken periodically from the bath for water uptake measurements, and then returned to the bath for subsequent mass uptake measurements.

## RESULTS and SUMMARY

From Fig.1, a linear relationship (dashed line) between the swelling of samples at saturation and the amount of water reabsorbed at saturation is noted (Case II reabsorption). Also, the two lines (solid and dashed lines) are parallel. This indicates the apparent free volume fraction occupied by the water in this structural adhesive remains constant at 2.00 % (with standard uncertainty 0.09 %) for the aging temperatures discussed ( $T \leq 45$  °C) in the reabsorption Case II. The constant fraction implies that the swelling of the adhesive at aging temperatures below 45 °C may have a negligible effect on the change of the apparent free volume. Also, although different swellings

have been observed for the samples hygrothermally aged at the same temperature in Case I (after saturation) and Case II, the apparent free volume probed by the water molecules for Case I samples is the same as that of Case II. In addition, this constant value is almost the same as the apparent free volume fraction (2.03 %, with standard uncertainty 0.09 %) probed by the same procedure in the absorption process for virgin samples. This identification indicates that the apparent free volume is not only independent of hygrothermal aging temperature but also hygrothermal aging history. Finally, this result is consistent with the previous argument [Chiang and Fernandez-Garcia, 1999] that two states of water molecules exist in this adhesive system, in which one population of water is considered to occupy apparent free volume of the adhesive, and the second population forms hydrogen bonded cluster.

Table 1 lists the diffusion coefficient ( $D$ ) obtained from the fit to the experimental data by using the non-Fickian diffusion model presented in the previous study [Chiang and Fernandez-Garcia, 1999]. In the Table 1, the maximum water uptake (saturation level) for different sorption processes with different hygrothermal aging temperatures are listed.

Table 2 presents the variation of glass transition temperature with hygrothermal temperature in the two cases of reabsorption process. Some results from the previous study on absorption and desorption are also listed in the Table 2. As shown in the table,  $T_g$  values for saturated samples from the two reabsorption processes exhibit practically identical values. This should be expected since almost the same saturation water content is measured in both reabsorption processes. It is also shown in the figure that the  $T_g$  value obtained for the saturated samples in absorption is almost same as that in the two reabsorption cases, although the specimens have different saturation levels. This is because the  $T_g$  depression depends on the water inside the apparent free volume but not the maximum amount of water uptake. And, this apparent free volume is a constant regardless of hygrothermal aging temperature and history. Consequently, the  $T_g$  depression is independent of the saturation amount.

The preliminary results show that the adhesive demonstrates a non-Fickian diffusion behavior with a dual-sorption mode regardless of hygrothermal aging history or the initial water content in the adhesive. The swelling observed by the reabsorption processes does not alter the apparent free volume of this adhesive system and  $T_g$  depression is independent of the final equilibrium water content of the system. These results are consistent with those in our previous paper, namely, that the water contained in the apparent free volume of the adhesive is the determining factor for the  $T_g$  depression.

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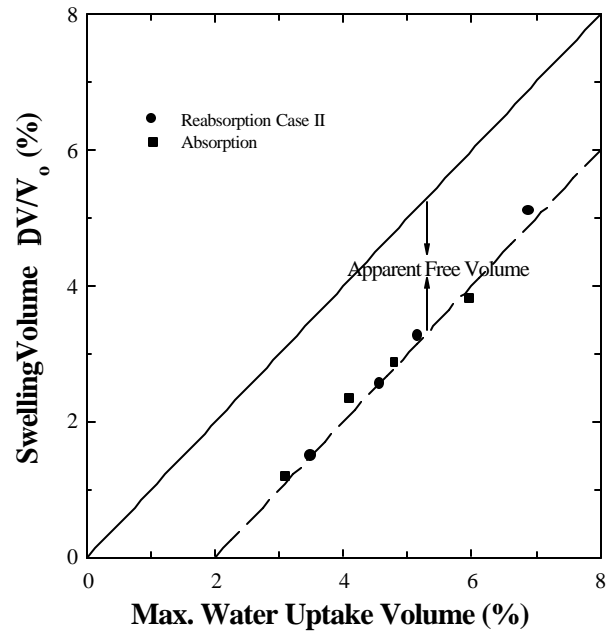


Fig.1 Swelling of samples versus the volume of saturated water uptake at different aging temperature for samples in absorption and Case II reabsorption processes

Table 1. Diffusion coefficients for adhesive at each temperature and process (values in the parentheses are standard uncertainties for the measurements)

Hygrothermal aging temperature (°C)	Absorption		Desorption at initial hygrothermal temperature		Reabsorption Case I		Reabsorption Case II	
	D ( $10^{-13}$ cm <sup>2</sup> /s)	M <sub>x</sub> (%)	D ( $10^{-13}$ cm <sup>2</sup> /s)	M <sub>x</sub> (%)	D ( $10^{-13}$ cm <sup>2</sup> /s)	M <sub>x</sub> (%)	D ( $10^{-13}$ cm <sup>2</sup> /s)	M <sub>x</sub> (%)
30	2.18 (0.024)	2.80 (0.062)	3.35 (0.037)	1.97 (0.084)	3.03 (0.039)	3.16 (0.088)	9.18 (0.101)	3.25 (0.081)
35	4.50 (0.053)	3.70 (0.093)	4.64 (0.049)	2.98 (0.080)	4.91 (0.054)	4.14 (0.119)	11.82 (0.130)	4.18 (0.113)
40	5.03 (0.045)	4.35 (0.130)	6.47 (0.074)	3.58 (0.086)	6.24 (0.072)	4.65 (0.102)	19.22 (0.208)	4.64 (0.138)
45	7.28 (0.091)	5.42 (0.147)	9.36 (0.092)	4.63 (0.102)	9.15 (0.118)	6.32 (0.158)	24.79 (0.268)	6.23 (0.185)

Table 2. Glass transition temperature for each process (the standard uncertainty for the  $T_g$  measurements is  $\approx 3$  °C)

Hygrothermal Aging Temperature (°C)	$T_g$ (°C)			
	Absorption	Desorption at initial aging temperature	Reabsorption Case I	Reabsorption Case II
30	64.0	75.8	65.1	60.3
35	62.2	77.7	63.2	61.7
40	62.7	76.2	64.4	61.5
45	64.5	77.9	64.9	62.2

\* $T_g$  for unexposed sample is 86.2 °C